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Summary report for the third year.

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Electronic Luminescence, Potential energy surfaces, Branching ratio, Surprisal analysis, Information theory, Inversion procedures, Structure-reactivity correlations, Linear free energy relations, Chemiluminescent ion-molecule reactions, Multiphoton dissociation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

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27 - ABSTRACT: THE FACTORS GOVERNING CHEMICAL REACTIVITY WITH SPECIAL REFERENCE TO THE ROLE OF ELECTRONIC ENERGY IN PROMOTING THE REACTION AND TO THE PRODUCTION OF ELECTRONICALLY EXCITED SPECIES ARE EXAMINED. THE PROBLEM IS STUDIED BOTH IN GENERAL TERMS (I.E., THE DEVELOPMENT OF THE REQUIRED THEORETICAL FRAMEWORK) AND IN APPLICATION TO SPECIFIC SYSTEMS. (AUTHOR)

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Electronic Excitation in Molecular Collisions:
Structural, Dynamic and Kinetic Considerations.

R.D./Levine
Principal Investigator
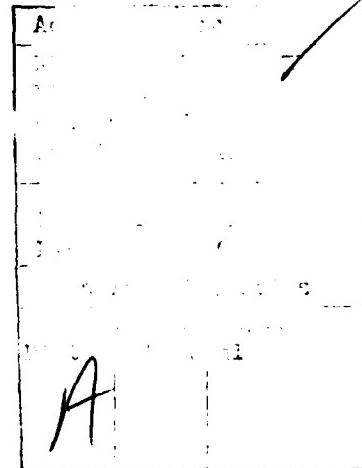
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[*]Arranged according to the 'Summary Questionnaire' of the
ONR Physics Program.

1. Principal Investigator

R.D. Levine
Professor of Physical and Theoretical Chemistry
The Hebrew University of Jerusalem.

2. Contract Description

The acquisition, storage and disposal of electronic energy by molecular collisions.

3. Scientific Problem

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

4. Technical Approach

Much of the work is based either directly or indirectly on the information theoretic approach to molecular collision theory, as pioneered and developed in Jerusalem.

5. Progress[*]

This report places the central attention on recent progress in multi-photon ionization because of the considerable impact that has already been made and because of the implications to the central theme of this proposal.

Progress in other directions has been reported in the semi-annual report (March 1981).

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[*]References are to the list of publications, paragraph 6 below.

The work carried out by Mr. A.S. Heilperin and Dr. P. Pfeifer is rapidly reaching completion and will be discussed in detail in the next report.

a.   Multiphoton Ionization: Introduction

The earliest evidence for multiphoton excitation of polyatomic molecules was the observation of electronically excited species. It was therefore deemed appropriate to develop an approach where the branching fractions for formation of all possible species, following multiphoton pumping, could be readily estimated. In particular, the method is eminently suitable for computing the fraction of electronically excited species, both neutral and ionic. As a test case we have selected to study the extensive fragmentation of polyatomic molecules which is observed following resonance enhanced multiphoton ionization. A simple statistical theory where the fragmentation pattern is governed by the mean energy uptake per parent molecule has been formulated and compared with experimental results for benzene. (The only input are the standard thermodynamic functions of all neutral and ionic dissociation products and the major uncertainties are in the heats of formation of some of the ions). By varying the mean energy absorbed it is found possible to span the range of different observed fragmentation patterns, from the production of primarily C_6 and C_4 ions at low energies up to the dominance of C_1 ions above 37 eV/molecule. A preliminary account has been published [11].

b.   Multiphoton Ionization: Experimental Tests of the Theory

The theory makes three specific predictions that can be tested in a computation-free manner:

(1) The fragmentation pattern of a given compound is governed only by the mean energy absorbed per molecule. We quote the abstract of the paper (Journal of Chemical Physics, in press) by Lichtin, Bernstein and Newton of Columbia University: "An experimental test of the Silberstein-Levine (SL) maximal-entropy theory of multiphoton ionization-fragmentation has been devised and applied to a diverse group of polyatomic molecules. The MPI fragmentation pattern of a given compound is strongly dependent upon the laser wavelength (which governs the "pathway" to the continuum) and the laser power density (and pulse energy). Nevertheless, it is found possible to obtain similar fragmentation patterns at several wavelengths (i.e. via different pathways) by adjusting the laser power so as to excite the molecule/ion system to the same average value of internal energy $<E>$. Data are presented for benzene, toluene, t-butylbenzene, triethylenediamine, quinuclidine and iodomethane, all of which tend to confirm the major premise of the SL theory that the branching fraction pattern is governed by the single parameter $<E>$." We have complemented this test by performing a computational study [18]. It was possible to well-reproduce the detailed, unit mass resolution observed fragmentation patterns.

(2) The theory predicts that at the same mean energy, different
isomers will have the same fragmentation pattern. This prediction was
met with considerable scepticism. Experimental tests were undertaken
at several laboratories, most notably by Professors M.E. El-Sayed
(UCLA; the C_6H_6 isomers) and R.N. Zare (Stanford; Azulene and Toluene).
We have just been informed by Professor Zare that his results support
our conclusion.

Experiments carried out at the Naval Research Laboratory by
Hudgens, Seaver and DeCorpo on 1,2-dichloroethane isomers also support
this conclusion.

(3) The most detailed prediction of the theory that can be checked
in a computation free manner is the energy distribution in the
products. (This includes, in particular, electronic energy which is
further discussed in subsection c below). Experiments are under way
in several laboratories. Preliminary results on the vibrational
distribution in C_2^* (from Professor Ogawa in Japan) seem to be in
very good accord.

c. <u>Multiphoton Ionization</u>: <u>The Production of Electronically Excited Species</u>
Reports of the observation of visible and UV luminescence following multi
photon pumping (using both ir and visible or UV photons) are becoming
increasingly common. In several instances (most notably, C_2 and CH) a
positive identification of the emitting species and level have been made
We have therefore undertaken a systematic survey of this phenomena.

Our computations [19] show a copious production of electronically excited species, Figure 1, already at quite moderate laser intensities. The concentration of the excited species is typically below that required for a complete population inversion. However, and as is well known, laser action requires only an inversion for the particular line of interest, and this can easily be the case. We are currently examining metal containing organic compounds (e.g. $Fe(CO)_5$) where we hope to be able to drive the system to large (absolute) population of excited species.

d. Multiphoton Ionization: Ion Pair Formation

As the very name indicates, the conventional wisdom is that the first process is ionization, to be followed by fragmentation. With some temerity we have recently [20] questioned this point of view. Our computations suggest that at least for polar molecules, e.g. CH_3Cl (but also non polar e.g. I_2) there is a very facile formation of ion pairs. At lower energies this pathway does appear to effectively compete with ionization.

This prediction is currently awaiting an experimental verification. If validated, it offers the following potentially interesting route to the production of excited neutral species: Even lower energy than the ion pair threshold are processes leading to electronically excited neutral fragments. Such processes require less input energy than ionization. We are currently looking for a promising test case.

6. <u>Publications</u>

<u>Published papers</u>

1. R.D. Levine, Free Energy of Activation: Definition, Properties and Dependent Variables, J. Phys. Chem. <u>83</u>, 159 (1979).

2. R.D. Levine and C.E. Wulfman, Energy Transfer to a Morse Oscillator, Chem. Phys. Letters <u>60</u>, 372 (1979).

3. R.D. Levine, An Information Theoretic Approach to Inversion Problems, J. Phys. <u>A13</u>, 91 (1980).

4. N. Agmon and R.D. Levine, Empirical Triatomic Potential Energy Surfaces Defined Over Orthogonal Bond Order Coordinates, J. Chem. Phys. <u>71</u>, 3034 (1979).

5. N. Agmon, An Analytical Approximation for the Number of States Along the Reaction Coordinate, Chem. Phys. <u>45</u>, 249 (1980).

6. E. Pollak and R.D. Levine, The Reactivity-Selectivity Principle: The Derivation of Bounds and A Computational Study, J. Chem. Phys. <u>72</u>, 2484 (1980).

7. E. Pollak and R.D. Levine, Statistical Theories for Molecular Collisions: A Maximum Entropy Derivation, J. Chem. Phys. <u>72</u>, 2990 (1980).

8. N. Agmon and R.D. Levine, Structural Considerations in Chemical Kinetics: Gas Phase H-Atom Transfer Reaction Series, Isr. J. Chem. <u>19</u>, 330 (1980).

9. N. Agmon, Is There A Nitroalkane Anomaly? J. Am. Chem. Soc. <u>102</u>, 2164 (1980).

10. G.L. Hofacker and R.D. Levine, On Maximizing the Information from an Indirect Experiment, Zeit. f. Naturf. <u>35a</u>, 490 (1980).

11. J. Silberstein and R.D. Levine, Fragmentation Patterns in Multiphoton Ionization: A Statistical Interpretation, Chem. Phys. Letts. <u>74</u>, 6 (1980).

12. E. Zamir, R.D. Levine and R.B. Bernstein, The Practice of Surprisal Inference: Products' State Distribution in the Chemiluminescent Ion-Molecular Reaction of $C^+ + H_2$, Chem. Phys. <u>55</u>, 57 (1981).

13. N. Agmon, Structure Reactivity Correlations, in "Molecular Structure and Dynamics" (Lectures in Honour of S. Lifson) edited by M. Balaban (International Science Services, Philadelphia 1980), pp. 155-170.

14. R.D. Levine, The Reactivity-Selectivity Principle, in "Molecular Structure and Dynamics" (Lectures in Honour of S. Lifson) edited by M. Balaban (International Science Services, Philadelphia 1980), pp. 129-

15. N. Agmon, From Energy Profiles to Structure-Reactivity Correlations, Int. J. Chem. Kinet. 13, 333 (1981).

16. R.D. Levine, Dynamical Symmetries and the Maximum Entropy Formulation of Collision Theory, Chem. Phys. Letts. 79, 205 (1981).

Papers accepted for publication

17. R.D. Levine, Invariance and the Distribution of Maximal Entropy.

18. J. Silberstein and R.D. Levine, Statistical Fragmentation Patterns in Multiphoton Ionization: A Comparison with Experiment.

19. N. Ohmichi, J. Silberstein and R.D. Levine, Production of Electronical Excited Fragments in Multiphoton Excitation.

20. N. Ohmichi, J. Silberstein and R.D. Levine, Ion Pair Formation in Multiphoton Fragmentation.

21. P. Pfeifer, All-Time vs. Asymptotic Reduced Dynamics and Entropy in Finite Quantum Systems.

7. Special circumstances

   n o n e

8. Budget

As allowed for in the budget, some of the funds allocated for post-doctoral

support were used to increase the fraction of the time that the programmer

spent on this project.

9. Personnel

R.D. Levine, Principal Investigator.

Dr. E. Keren, postdoctoral fellow, left Oct. 1979.

Dr. J. Rookstool, postdoctoral fellow, left July 1981.
   U.S. citizen from Dallas, Texas, worked on implementing surprisal
   synthesis as a practical computational procedure.

Dr. P. Pfeifer, postdoctoral fellow.

Dr. N. Ohmichi, postdoctoral fellow working on multiphoton ionization.

Mr. N. Agmon, advanced graduate student, received his Ph.D. June 1981.
    Mr. Agmon's Ph.D. thesis, which represents work supported by
    this proposal (cf. publications 4,5,8,9,13,15) has been judged
    by the Graduate Committee as the best science thesis of the
    year, and awarded the Katzir Prize in the presence of (former)
    Vice-President Mr. W. Mondale.

Mr. A.S. Heilperin, advanced graduate student.

Mr. E. Zamir, graduate student.

Mr. J. Silberstein, graduate student working on multiphoton ionization.

Mr. H. Almagor, programming assistant.

10. Other Current or Requested Federal Grants and Other Contract Support
     of R.D. Levine at the Hebrew University

     a. Studies in Molecular Disequilibrium

        The U.S.-Israel Binational Science Foundation, April 1981 - March 1982,

        $\sim$ \$ 8000. J.L. Kinsey, I. Oppenheim, R. Silbey and J.I. Steinfeld

   cooperating investigators.

     b. Multiphoton Ionization

        The U.S.-Israel Binational Science Foundation, April 1981 - March 1982,

        $\sim$ \$ 9000. R.B. Bernstein cooperating investigator.

     c. Algebraic Methods in Collision Theory

        The U.S.-Israel Binational Science Foundation, April 1981 - March 1982,

        $\sim$ \$ 8000. C.E. Wulfman cooperating investigator.

        (a), (b) and (c) are lower cost grants primarily to enable the
cooperating investigators to spend time with the research group of R.D. Levine
in Jerusalem. Grant (a) is now in its final year.

C$_2^*$ Population in Fragmentation of C$_2$H$_2$

% Population / degeneracy

20

15

10

5

0

X$^3\Pi$u

X$'\Sigma$g$^+$

A$'^3\Sigma$g$^-$

b$'\Pi$u

A$^3\Pi$g

c$'\Pi$g

T–T   A$^3\Pi$g $\longleftrightarrow$ X$'^3\Pi$u   Swan

A$'^3\Sigma$g$^-$ $\longleftrightarrow$ X$'^3\Pi$u   Ballik R̶̶̶̶

S–S   b$'\Pi$u $\longleftrightarrow$ X$'\Sigma$g$^+$ Phillips

c$'\Pi$g $\longleftrightarrow$ b$'\Pi$u   Deslandres
d'Azambuja

5   10   15   20   25   30   35

$\langle E \rangle$ eV
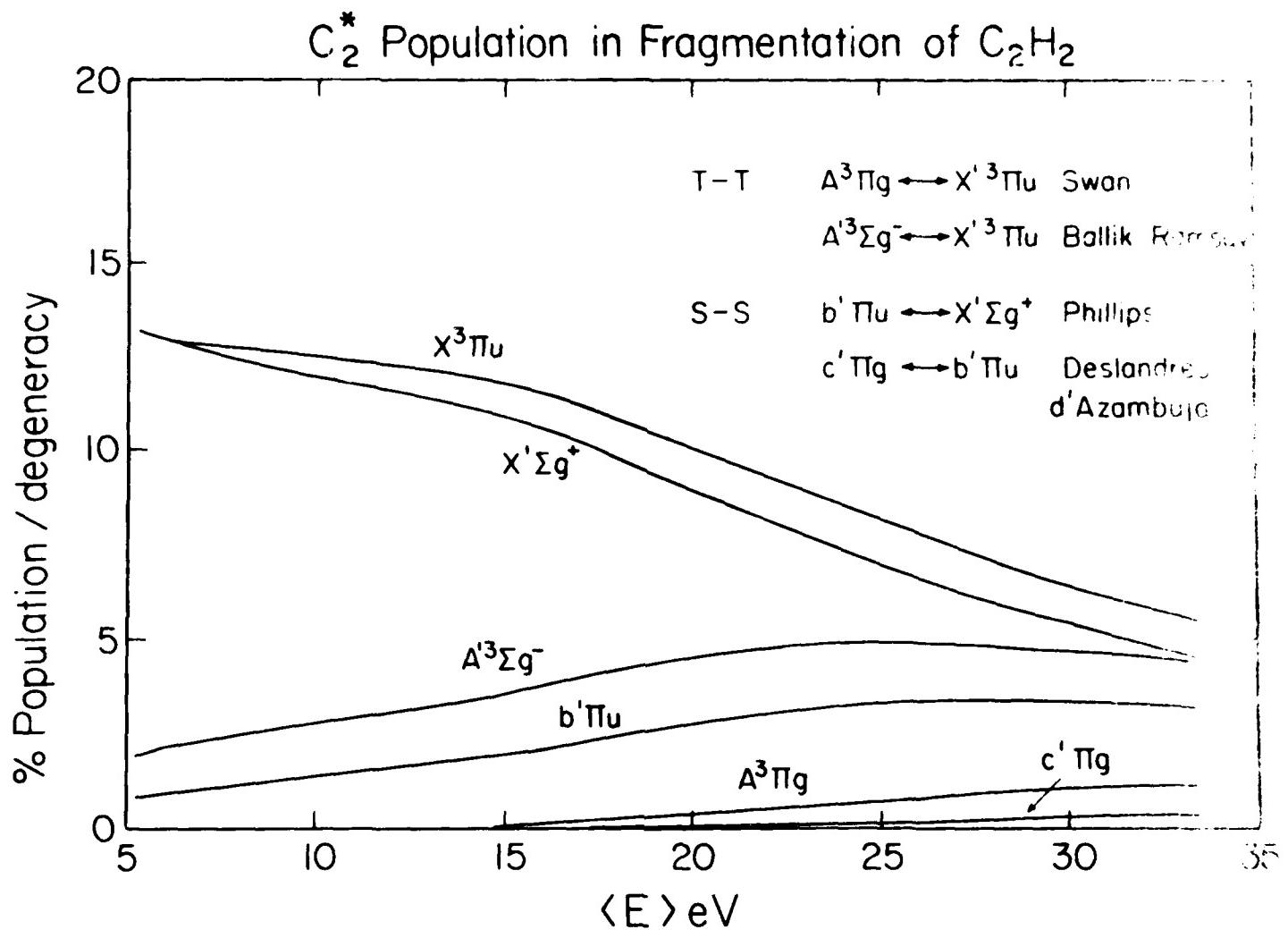
The distribution of C$_2$ electronic states as a function of the mean energy (absorbed from the laser) per C$_2$H$_2$ molecule. Shown is the relative population divided by the degeneracy of the electronic state.

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